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Objectives

Considerable current research has been devoted to the development of linearly conjugated organic systems (e.g., conjugated polymers) for applications in, for example, electronics. Linearly conjugated systems have also been examined as conducting units in single molecule devices. Considerably less work has been done on the development of so-called cross-conjugated systems,¹ which manifest quantum interference effects. On one level, this results in limited conjugation lengths (e.g., for the development of UV-emitting polymers). However, cross-conjugated systems have also been proposed as functional units for the creation of single-molecule devices such as transistors;² cross-conjugation is not functionally equivalent to “broken” conjugation. Instead, the conductance through cross-conjugated units should be very sensitive to external influences.

The overall goal of this project was to develop a class of tetrabenzo[18]cyclynes as a platform for the investigation of structure property effects on cross-conjugated systems, as shown in Figure 1. This “push-pull” macrocyclic framework was chosen because it is rigid and structurally well-defined. Consequently, we expected interpretation of the results (aided by computational modeling) to be comparatively straightforward. The cyclic structure was also chosen as a way to incorporate cross-conjugated units into functional columnar materials, in particular liquid crystals. Finally, we envisioned that the results would be more relevant in the long term: the shape-persistent structure should be inherently better suited to incorporation into networks (i.e., “wiring” multiple devices together), and two-dimensional self-assembly of compounds with a similar footprint has been extensively demonstrated.³

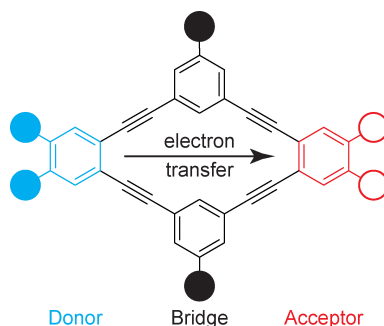


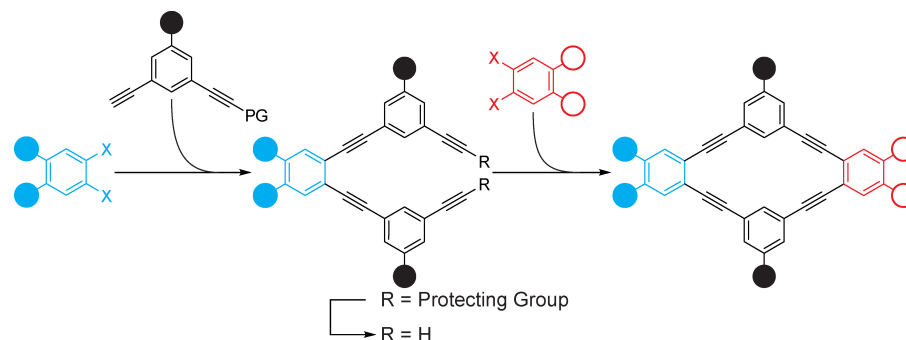
Figure 1. Basic structure of the tetrabenzo[18]cyclynes investigated in this project.

Accomplishments by Specific Aim

Specific Aim 1: Development of Synthetic Methods

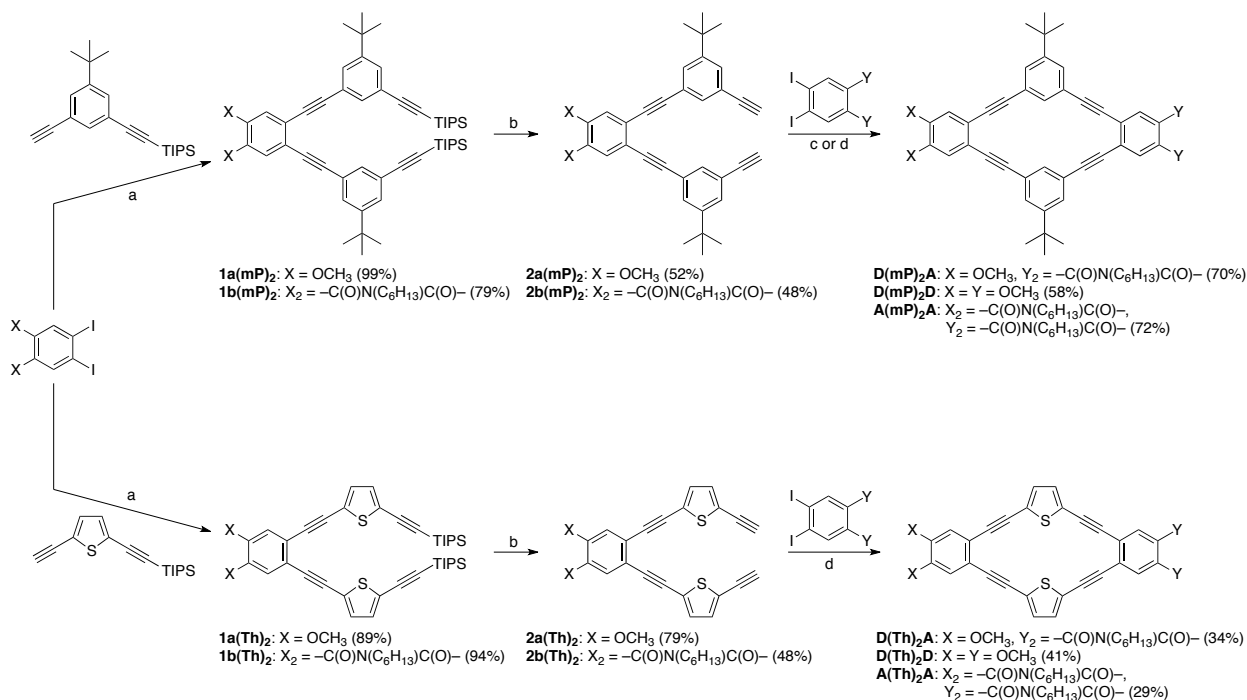
This project was funded through the AFOSR program on *Molecular Design and Synthesis*, prior to its dissolution in 2010. Consequently, a significant fraction of the project was spent on the development of methods for the synthesis of push-pull macrocycles and related structures.

While two synthetic approaches to the tetrabenzo[18]cyclyne core were known prior to the start of this project, neither was appropriate for the target compounds as the syntheses were either too involved⁴ or did not allow the appropriate substitution pattern.⁵ Thus, the first challenge was to develop a method that would allow the final macrocycles to be assembled using the same three steps used for more conventional acyclic donor-bridge-acceptor compounds, as shown in Scheme 1.



Scheme 1. General synthetic approach to tetrabenzo[18]cyclynes.

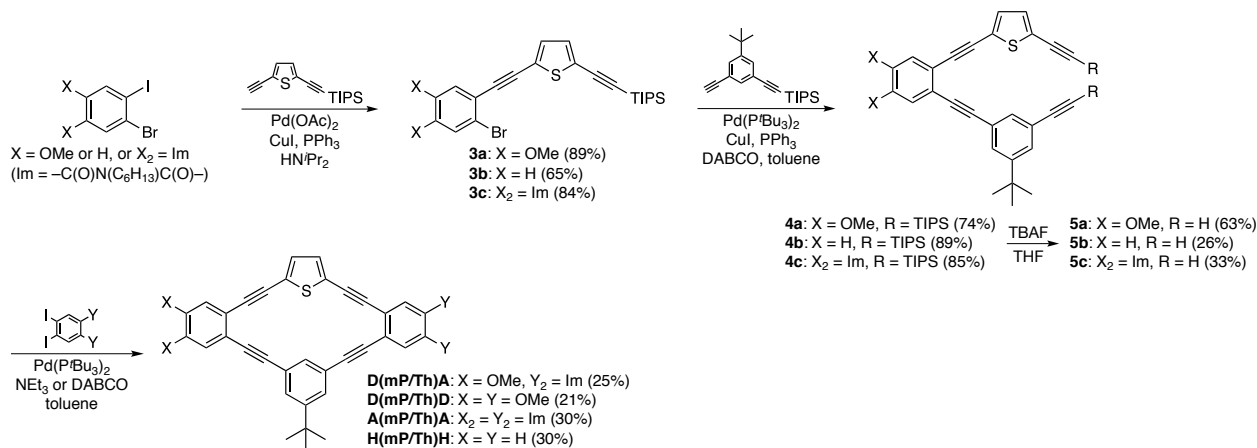
Two series of compounds were initially targeted: the original *m*-phenylene-based macrocycles and a series of macrocycles with 2,5-thiophene bridges (the 2,5-thiophene unit is linearly conjugated, and thus serves as an important comparison), as shown in Scheme 2. The key step was the macrocyclization, as the conditions had to be chosen carefully to avoid polymerization. After optimization, copper-free Sonogashira conditions using $\text{Pd}(\text{P}^t\text{Bu}_3)_2$ as the catalyst were identified. Yields for this key step for the *m*-phenylene-based macrocycles are very good (e.g., 72% for **D(mP)₂A**), while those for the 2,5-thiophene are modest. This difference is readily explained by the poor fit of the thiophenes within the macrocyclic framework.



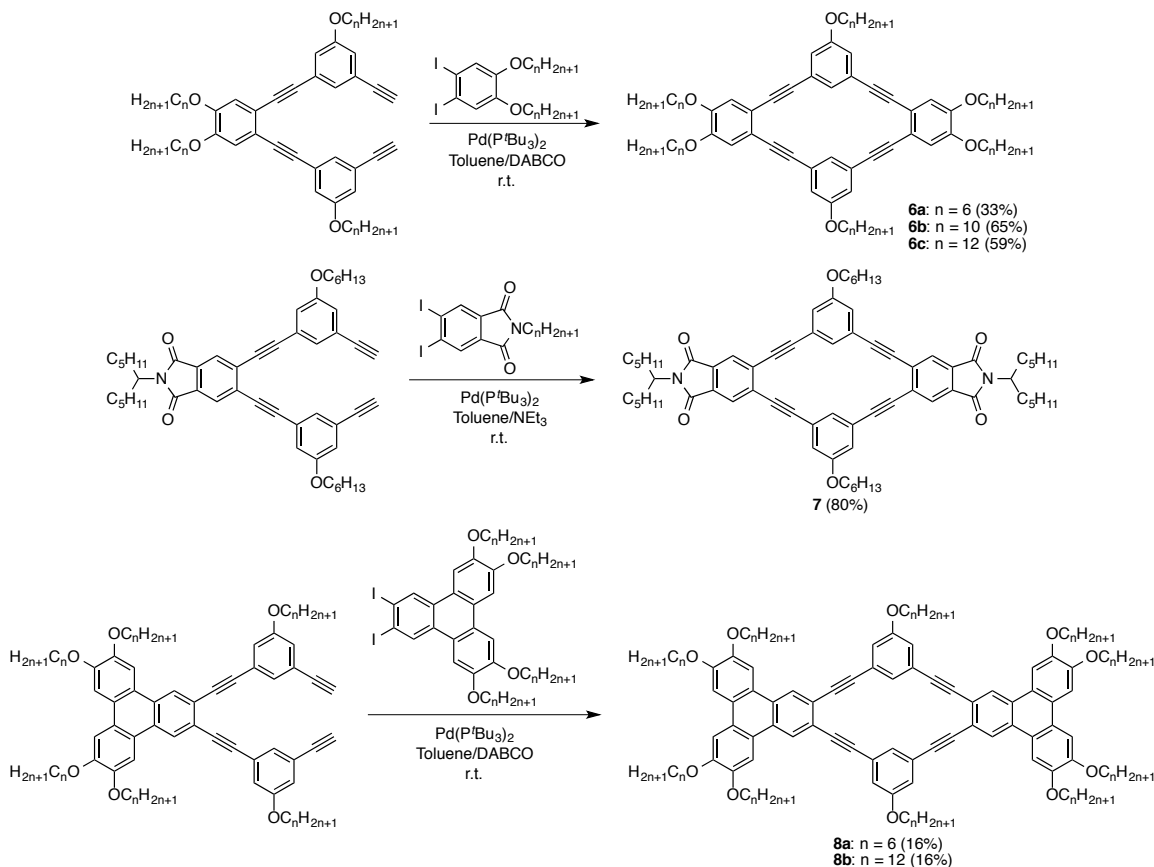
Scheme 2. Synthesis of push-pull macrocycles and symmetrical variations. Reagents and conditions: (a) $\text{Pd}(\text{OAc})_2$, PPh_3 , CuI , HN^iPr_2 ; (b) TBAF, THF; (c) $\text{Pd}(\text{PtBu}_3)_2$, NEt_3 , toluene (**D(mP)₂A** and **A(mP)₂A**); (d) $\text{Pd}(\text{P}^t\text{Bu}_3)_2$, DABCO, toluene (**D(mP)₂D**, all thiophenes).

We have also found that these conditions work well for other variations on the tetrabenzo[18]cyclyne theme. Specifically, the two bridges can be combined within single compounds to explore the effect of multiple conjugated pathways bridging individual electron-rich and electron-poor moieties, as shown in Scheme 3. Yields for the key macrocyclization step

are comparable to those of the bisthiophene macrocycles (e.g., **D(Th)₂A**), again because the 2,5-thiophene are not a perfect geometrical match for the rigid macrocyclic framework.

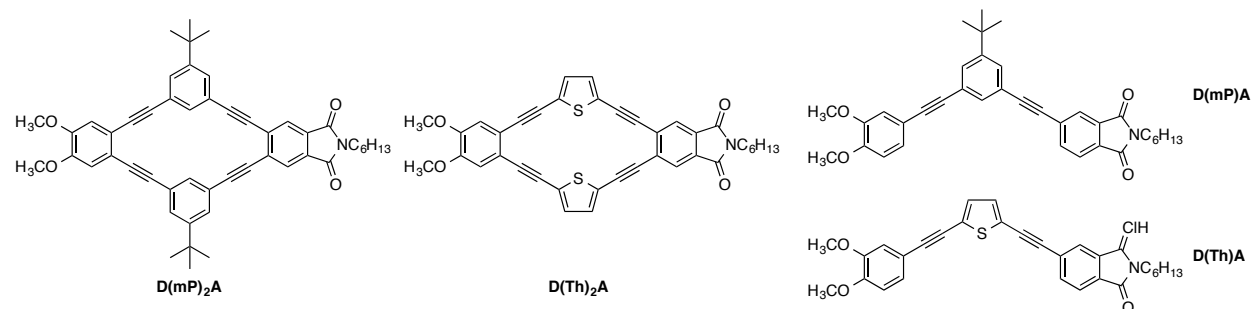


As part of our effort to explore the incorporation of tetrabenzo[18]cyclines into liquid crystals (see below), additional compounds were synthesized with various patterns of side-chains along the exteriors and various core structures, as shown in Scheme 4. Of course, substantial effort was devoted to synthesizing the precursors to these molecules, but these syntheses are relatively straightforward and are reported in full in our publications and theses.



Specific Aim 2: Characterization of Electronic Structure

The synthesized push-pull compounds (i.e., **D(mP)₂A**, **D(Th)₂A**, **D(mP/Th)A**) offer two unusual features to their structures: the cross-conjugation of the *m*-phenylene bridges, and the multiple conjugation paths linking the donor and acceptor units. UV-vis and fluorescence spectroscopy of the various compounds was used to investigate the effect of these structural variations on charge-transfer through the various combinations of bridges.



Spectra of the various compounds, along with those for acyclic control compounds **D(mP)A** and **D(Th)A**, are shown in Figure 2. In all cases, the shapes of the absorbance spectra are independent of solvent, indicating that excitation does occur to a relatively nonpolar state. Conversely, the fluorescence spectra are strongly solvent dependent, indicating that emission occurs from a much more polar charge-transfer state. Thus, the photophysics of these compounds, in polar solvents, can be broadly understood by the simple three-state model shown in Figure 3.

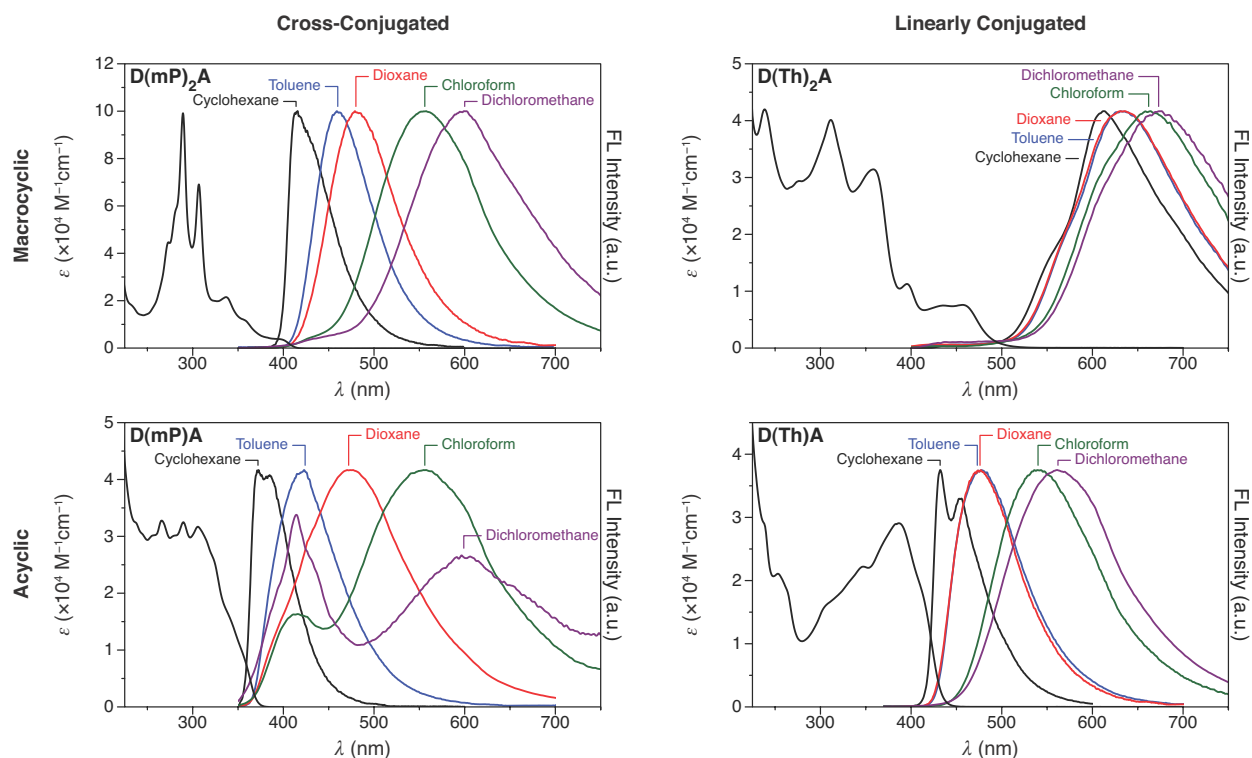


Figure 2. UV-vis (left, cyclohexane) and fluorescence (right) spectra of push-pull compounds.

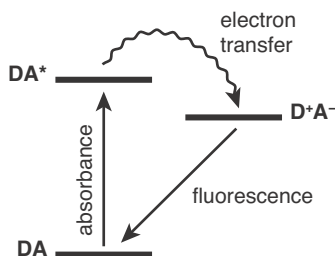


Figure 3. Three-state photophysical model expected for push–pull macrocycles.

The photophysical properties of the compounds were further evaluated by Lippert–Mataga analysis of the fluorescence solvatochromism and measurement of quantum yields and fluorescence lifetimes. Key properties for the symmetrical macrocycles and model compounds are given in Table 1. From these data, radiative (k_r) and non-radiative (k_{nr}) rate constants were calculated for the decay of the charge-transfer state.

Table 1. Photophysical properties of symmetrical macrocycles and associated model compounds.

	μ_e (D) ^a	Solvent ^b	Φ_f	τ_f (ns)	k_r ($\times 10^8 \text{ s}^{-1}$)	k_{nr} ($\times 10^8 \text{ s}^{-1}$)
D(mP)₂A	48	Cy	0.48	6.7	0.71	0.77
		Diox	0.31	22.2	0.14	0.31
		DCM	0.021	5.0	0.04	2.0
D(mP)A	48	Cy	0.40	1.5	2.7	4.1
		Diox	0.26	16.7 ^d	0.16	0.44
		DCM	<0.005	n.d.		
D(Th)₂A	25 ^c	Cy	0.017	2.3	0.08	4.3
		Diox	0.02	2.3	0.09	4.3
		DCM	0.005	1.0 ^e	0.05	10
D(Th)A	33	Cy	0.29	0.52	5.5	13
		Diox	0.19	0.56	3.4	15
		DCM	0.11	0.62	1.8	14
D(mP)₂D		Cy	0.63	3.3	1.9	1.1
A(mP)₂A		Cy	0.49	5.5	0.90	0.93
D(Th)₂D		Cy	0.008	1.1	0.07	9
A(Th)₂A		Tol	0.014	2.1 ^f	0.07	4.7

^a Calculated from Lippert–Mataga plots for binary mixtures of cyclohexane and dichloromethane. ^b Cy = cyclohexane, DCM = dichloromethane, Tol = toluene. ^c Based on the linear portion at the high Δf region of the Lippert–Mataga plot. ^d Double exponential fit: $\tau_1 = 21.5 \text{ ns}$ (73%) and $\tau_2 = 3.7 \text{ ns}$ (27%). ^e Double exponential fit: $\tau_1 = 0.85 \text{ ns}$ (87%) and $\tau_2 = 2.3 \text{ ns}$ (13%). ^f Double exponential fit: $\tau_1 = 1.8 \text{ ns}$ (86%) and $\tau_2 = 3.8 \text{ ns}$ (14%).

From these data, two key conclusions can be drawn. First, the cross-conjugated *m*-phenylene bridge does indeed appear to slow charge recombination. For example, τ_f for **D(mP)A** is roughly 30-fold longer than **D(Th)A** in dioxane, deriving from a large decrease in both its radiative and non-radiative decay rates. This property was largely expected based on literature precedent.⁶ Perhaps more interestingly, the pairing of the conjugated bridges leads to greatly decreased radiative and non-radiative decay rates, even for the linearly conjugated 2,5-thiophene bridges (i.e., **D(Th)₂A** vs **D(Th)A**). The reduction in k_{nr} likely derives from the increased rigidity of the macrocyclic structures, leading to less efficient vibrational deactivation. The decrease in k_r , however, must reflect a reduction in the electronic coupling between the charge-transfer and ground states. This property is uniquely derived from the two-dimensional design of the compounds, and, to our knowledge, such architectures with paired bridges had not been previously observed.

This result is counterintuitive: one might expect, for example, that the inclusion of a second conjugated “wire” between the donor and acceptor sides of the molecule would increase the rate of charge transfer. To better understand this phenomenon, time-dependent density functional theory (TD-DFT) calculations were performed for simplified model structures, shown in Figure 4 for **D(Th)₂A** and **D(Th)A**. As expected, the HOMOs for the push–pull compounds are localized largely on the donor (veratrole) sides of the compounds, and the LUMOs are localized on the phthalimide sides of the compounds. The time-dependent calculations do an excellent job of reproducing the UV–vis spectra of the compounds (excited-state geometry optimizations have not been performed, so the fluorescence spectra have not been calculated). Inspection of the frontier molecular orbitals suggests that the key is the symmetry of the compounds (the TD-DFT calculations support the assignment of a charge-transfer HOMO–LUMO transition to the fluorescence behavior). On pairing the bridges, the charge-transfer transition becomes symmetry forbidden. The effect of symmetry on the electronic coupling is, of course, a straightforward consequence of the physics of charge transfer and has been previously described in real molecules.⁷ What is unique here is the accessibility of this phenomenon through the design of these paired-bridge structures. As modification of the electronic coupling is important to the development of transistors, these motifs could be used in future single molecule devices.

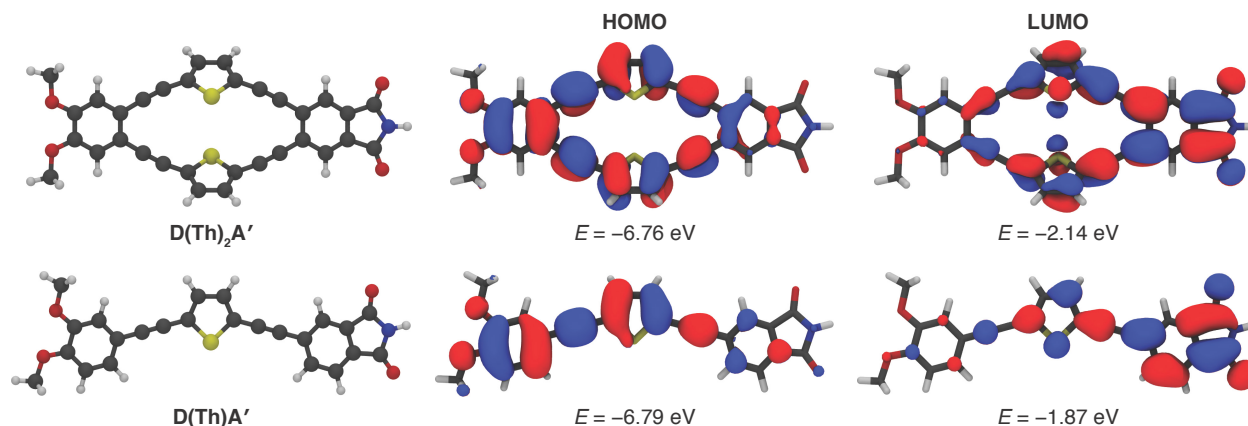


Figure 4. Frontier molecular orbitals of **D(Th)₂A** and **D(Th)A**. The structures are simplified through the replacement of C₆H₁₃ with H.

The photophysics of these compounds has been investigated further in collaboration with Nicole Dickson-Karn at Ohio Northern and the Center for Chemical and Biophysical Dynamics at Ohio State. Femtosecond spectroscopy has allowed charge-separation rates to be measured. Interestingly, the pairing of the bridges appears to increase the rate of charge separation in **D(mP)₂A** compared to **D(mP)A**, while decreasing the rate of charge separation. These experiments are currently ongoing.

The properties of mixed-bridge compound **D(mP/Th)A** were evaluated in order to further examine the interaction between conjugated bridges in two dimensional π -systems. As shown in Figure 5, the steady-state spectra are qualitatively similar to those of the symmetrical macrocyclic compounds, and the behavior is again qualitatively described by the model in Figure 3. The photophysical properties again suggest the unusual behavior of these two-dimensional conjugated systems. Curiously, the steady-state fluorescence spectra are a good match for the acyclic **D(Th)A** (similar quantum yields, similar Lippert–Mataga analysis), whereas the UV–vis spectra closely resemble those of the symmetrical macrocycle **D(Th)₂A**. Consideration of the fluorescence lifetimes, in combination with TD-DFT calculations, suggests that the two bridges

in this compound do interfere with each other by analogy with the symmetrical compounds, despite their very different natures (cross- vs linearly conjugated). The key result is that neither the analogous acyclic (**D(mP)Th** and **D(Th)A**) nor the symmetrical macrocyclic (**D(mP)₂A** and **D(Th)₂A**) push-pull compounds predict the behavior of the mixed-bridge compound, emphasizing the inherent complexity of these two-dimensional conjugated systems.

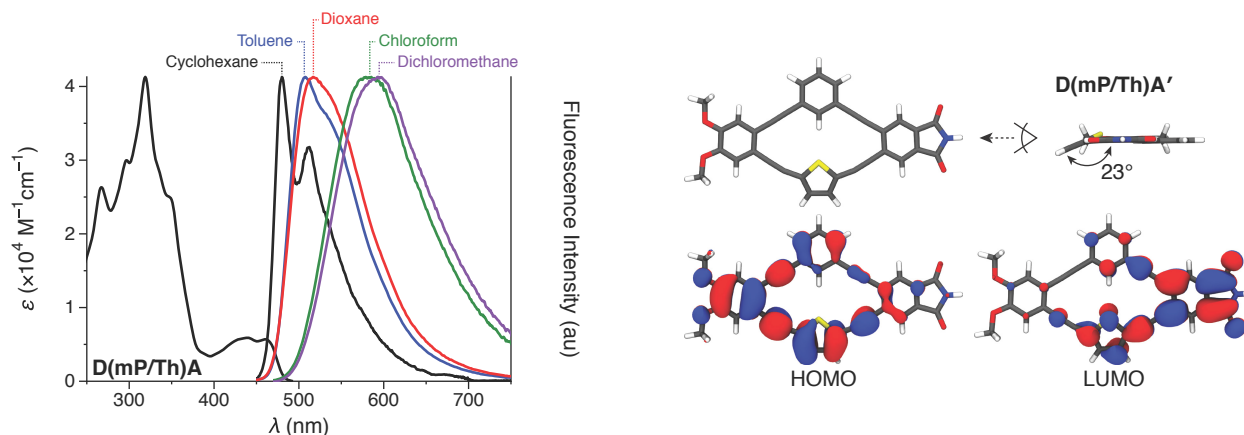
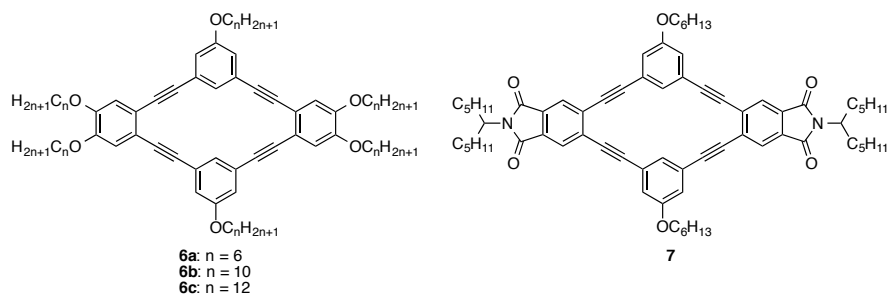


Figure 5. Left: photophysical properties of **D(mP/Th)A**. Right: DFT-optimized geometry and FMOs for simplified structure **D(mP/Th)A'**.

Specific Aim 3: Self-Assembly of Columnar Materials

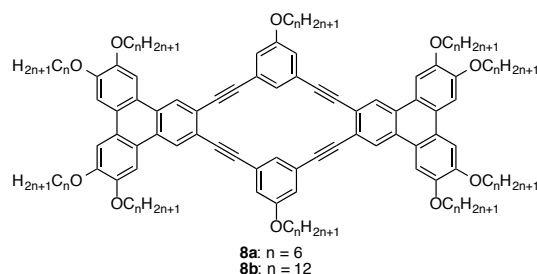
One of the advantages of working with macrocyclic materials (as opposed to more common acyclic donor-bridge-acceptor structures) is the possibility of incorporating them into functional columnar materials. For example, one long-term goal is to use the (cross-)conjugated bridges to control intramolecular charge transport, and then columnar stacking to exploit this phenomenon in photovoltaics.

In this project, columnar liquid crystals were targeted, as phenylene ethynylene macrocycles have been used as discotic mesogens in the past.^{8,9} We initially targeted the series of alkoxy-substituted compounds **6a**, **6b**, and **6c**. Unfortunately, evaluation of these compounds by polarized optical microscopy and differential scanning calorimetry showed no evidence of liquid crystallinity despite relatively low melting points for the higher homologues (melting points of 183, 115, and 100 °C for **6a**, **6b**, and **6c**, respectively). Compound **7** was examined because its electron-deficient phthalimide units could enhance aromatic stacking interactions within a column. This compound also failed to exhibit liquid crystalline behavior, however (decomposition at ~240 °C).



The final set of compounds examined for columnar self-assembly were triphenylene-based compounds **8a** and **8b**. The much larger aromatic surfaces of these compounds were expected to

promote aromatic stacking interactions, although an interesting aspect of their design is their unusual extended, oblong shape. They also incorporate more technologically relevant chromophores (the triphenylenes) bridged by the *m*-phenylene subunits.



The UV-vis and fluorescence spectra of **8a** and immediate trimer precursor **9a** suggests that there is limited electronic interaction between the two triphenylene units through the *m*-phenylene bridges. Indeed, the fluorescence lifetimes ($\tau_f = 5.2$ vs 5.7 ns for **8a** and **9a**, respectively) and quantum yields ($\Phi_f = 0.62$ vs 0.55) are also similar. Unfortunately, this compound is not electrochemically well-behaved, precluding the examination of charge delocalization through the *m*-phenylene bridges. While compound **8a** was not found to exhibit mesophases (m.p. 75°C), its ^1H NMR signals were found to exhibit strong upfield shifts with increasing concentration, indicating aromatic stacking in solution, as shown in Figure 7. Smaller compounds **6a–c** and **7** do not exhibit such behavior. The chemical shifts gave a very good fit to a standard indefinite association model with a (relatively large) association constant of $K_{eq} = 425 \pm 10 \text{ M}^{-1}$ in CDCl_3 . In contrast to most other macrocycles or aromatics examined for self-assembly in solution, the oblong shape of these compounds allows us to explore the effect of shape anisotropy on solution-phase columnar self-assembly. Interestingly, not all of the proton chemical shifts respond equally to increasing concentration. Comparison with DFT NMR simulations on model dimer complexes suggests that the NMR data are consistent with closely aligned molecular long axes and a $\sim 4 \text{ \AA}$ offset between stacked compounds (Figure 7). To the best of our knowledge, this is the first time DFT calculations have been used to interpret solution-phase stacking behavior in this way. Compound **8b** is currently being prepared to test for liquid crystalline behavior as a final step before publication.

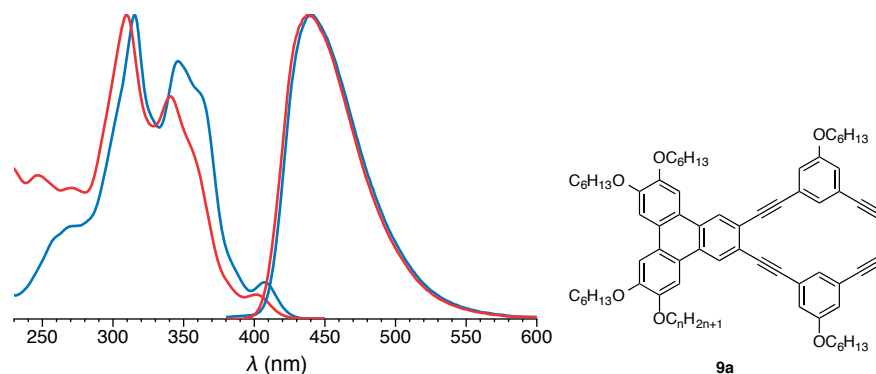


Figure 6. UV-vis (left) and fluorescence (right) spectra of **8a** (blue) and **9a** (red).

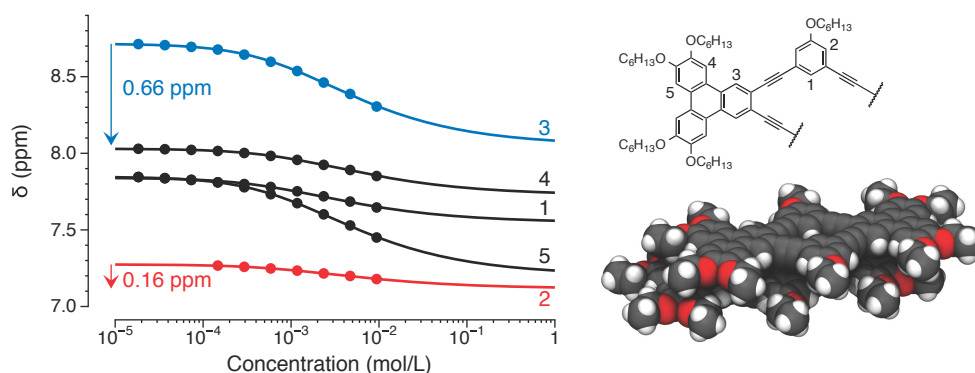


Figure 7. Left: Concentration-dependent ^1H chemical shifts for compound **8a** (CDCl_3); the solid lines represent fits to an isodesmic indefinite association model. Bottom right: offset stacking geometry consistent with the chemical shift changes.

Other Work

In addition to the primary work described above, resources purchased with grant FA9550-10-1-0377 (the license for *Gaussian 09*, the RCS 40 cooling unit for the differential scanning calorimeter, and the lifetime fluorometer) have been leveraged for some other research projects and collaborations. In particular, they have been used as part of work on the folding of conjugated oligomers in solution, computational modeling of dyes for dye-sensitized solar cells, and characterization of new liquid crystalline materials with board-like structures. AFOSR support has been acknowledged in the relevant publications (listed below).

Publications Acknowledging Grant FA9550-10-1-0377

- (1) Mathew, S. M.; Hartley, C. S. Parent *o*-phenylene oligomers: Synthesis, conformational behavior, and characterization. *Macromolecules* **2011**, *44*, 8425–8432 (10.1021/ma201866p).
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- (11) Dickson-Karn, N. M.; Leu, W. C. W.; Hartley, C. S. Manuscript in preparation.
- (12) Chu, M.; Scioneaux, A. N.; Hartley, C. S. Manuscript in preparation.

Presentations Acknowledging Grant FA9550-10-1-0377

- (1) C. S. Hartley, “ortho-Phenylenes and push–pull macrocycles: Unusual organic nanoarchitectures”. Invited speaker, Southern Illinois University, Carbondale, Illinois, March 1, 2013.
- (2) C. S. Hartley, “ortho-Phenylenes and push–pull macrocycles: Unusual organic nanoarchitectures”. Invited speaker, Kent State University, Liquid Crystals Institute, Kent, Ohio, November 14, 2012.
- (3) C. S. Hartley, “ortho-Phenylenes and push–pull macrocycles: Unusual organic nanoarchitectures”. Invited speaker, Wright–Patterson Air Force Base, April 25, 2012.
- (4) C. S. Hartley, “ortho-Phenylenes and push–pull macrocycles: Unusual organic nanoarchitectures”. Invited speaker, University of Nevada, Reno, Nevada, February 16, 2012.
- (5) C. S. Hartley, “ortho-Phenylenes and cross-conjugated macrocycles: Unusual architectures for organic nanotechnology”. Invited speaker, Otterbein University, Westerville, Ohio, September 20, 2011.
- (6) W. C. W. Leu and C. S. Hartley. “Donor–acceptor substituted shape persistent macrocycles.” Poster presentation, 14th International Symposium on Novel Aromatic Compounds, University of Oregon, Eugene, OR, July 24–29, 2011.
- (7) C. S. Hartley, Jian He, and Ashley N. Scioneaux, “Synthetic approaches to board-like mesogens: Dibenzo[*fg,op*]naphthalenes and tetrabenzocyclynes”. Poster presentation, 2011 Gordon Conference on Liquid Crystals, Mount Holyoke College, Massachusetts, June 19–24, 2011.
- (8) A. Scioneaux and C. S. Hartley. “Liquid crystalline tetrabenzo[18]cyclynes.” Poster presentation, 38th Annual Meeting of the National Organization for the Professional Advancement of Black Chemists and Chemical Engineers. Houston, TX, April 19–22, 2011.
- (9) C. S. Hartley, “ortho-Phenylenes and cross-conjugated macrocycles: Unusual molecular architectures for single-molecule devices”. Invited speaker, University of Evansville, Evansville, Indiana, October 29, 2010.
- (10) C.-W. Leu and C. S. Hartley. “Donor–acceptor cross-conjugated macrocycles.” Poster presentation, 240th ACS National Meeting, Boston, Massachusetts, August 22–26, 2010.
- (11) A. N. Scioneaux and C. S. Hartley. “Liquid crystalline tetrabenzo[18]cyclynes.” Poster presentation, 240th ACS National Meeting, Boston, Massachusetts, August 22–26, 2010.

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